

LIQUEFACTION BEHAVIOR OF HIGH-SULFUR LIGNITES

Ana B. Garcia and Harold H. Schobert

Fuel Science Program

The Pennsylvania State University

University Park, PA 16802

INTRODUCTION

Previous work in this laboratory has investigated the hydrodesulfurization of Mequinenza (Spanish) lignite, a coal which is of interest for its remarkable organic sulfur content of about 11% on a daf basis. In experiments using impregnated molybdenum catalysts, sulfur removals of up to about 70% were obtained (1,2). In an ideal process configuration, the hydrodesulfurization reaction would remove the organic sulfur as H_2S , leaving a sulfur-free or low-sulfur char suitable for combustion. However, it is inevitable that the reaction of a highly reactive lignite with hydrogen in the presence of a good hydrogenation catalyst will produce some liquids as by-products. In fact, in the experiment in which a sulfur reduction of 70% was achieved, 48% of the lignite was converted to liquid products, although most of the sulfur removed did appear as H_2S . This behavior prompted an examination of the liquefaction reactivity of this lignite, with particular concern for the formation of liquids at relatively mild conditions and short reaction times.

Given's study of the liquefaction behavior of 104 high volatile bituminous coals included coal samples of up to 7.3% total sulfur (dry basis) (3). Examination of the data by cluster analysis showed that a factor representing sulfur had a major role in separating the coals into statistically separate groups. Subsequent work, using a set of 26 high volatile bituminous coals with a maximum sulfur content of 7.9% (dry basis), showed no significant relationships of the yields of oils, asphaltenes, or gas to sulfur content (4). The highest organic sulfur content of the coals used in that work was 3.3% (dry basis). The final comment in the 1988 paper (4) was that, "the role of sulphur in coals clearly merits further intensive study."

The work reported here used coals of different rank and much milder reaction conditions. Furthermore, a much smaller sample set was used. Therefore, our results are not intended to be a direct extrapolation of previous work (3,4), but rather represent a collateral line of investigation. The results presented here offer some insights into the exploitation of the relatively weak C-S bond for obtaining good liquids yields at mild conditions which might be typical of the low-temperature stage of a temperature-staged liquefaction system.

EXPERIMENTAL

Three lignites were used in this work: Hagel seam lignite from the United States, Cayhiran lignite from Turkey, and the Spanish Mequinenza lignite mentioned above. Some of the characteristics of these lignites are shown in Table 1. The principal criterion for the choice of these lignites was to obtain as wide a range of organic sulfur contents as possible. A secondary consideration, having first obtained the desired organic sulfur contents, was to obtain lignites with reasonably comparable carbon and hydrogen contents.

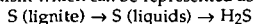
The procedure for conducting the reactions was the same regardless of the gas atmosphere or whether a catalyst was used. All reactions were carried out in microautoclave reactors (tubing bombs) of nominal 30 mL capacity. A 5 g lignite sample of dry lignite was used. No solvent was used in these experiments. The reactor was flushed three times with the desired gas, either nitrogen or hydrogen, before being pressurized to 6.9 MPa. The pressurized reactor was then immersed in a sandbath preheated to 275° C. The reactor was subjected to vertical oscillation of 2.5 cm at 200 cycles/min for 30 min. At the end of an experiment the reactor was rapidly quenched by immersion in cold water.

The cooled reactor was vented into a glass expansion bulb from which samples could be withdrawn for gas chromatographic analysis. The reactor contents were washed with tetrahydrofuran (THF) into a dry Soxhlet thimble and were then extracted with THF for about 24 hr under nitrogen. The THF was removed from the extract by rotary evaporation. The solid residue was dried at 100° for 18-20 hr before weighing. The gas yield was calculated by difference from the weights of the liquids and the THF-insolubles.

For experiments in which a catalyst was used, the lignites were impregnated with reagent grade ammonium tetrathiomolybdate, $(\text{NH}_4)_2\text{MoS}_4$. An amount of this salt sufficient to give a 1% molybdenum loading (expressed on a daf basis as elemental molybdenum, not the molybdate salt) was dissolved in sufficient distilled water to give a 1:1 lignite:water ratio. The lignite was slurried in the aqueous solution and stirred for at least 2 hr. Excess water was removed by vacuum freeze drying to a lignite moisture content below 1%. Typically the impregnation procedure was carried out with a large enough batch of lignite to suffice for a series of experiments. The dried, impregnated lignites were stored under nitrogen.

RESULTS AND DISCUSSION

An analysis of the yields of sulfur-containing liquids and H_2S , and of the selectivities to these products, as functions of conversion suggests that the net hydrodesulfurization process for the Mequinenza lignite occurs via a sequential mechanism which can be represented as



This analysis has been discussed previously (5) and is presented in detail elsewhere (6). Assuming that the reaction follows pseudo-first order kinetics allows calculation of the apparent activation energy for hydrodesulfurization by the standard Arrhenius approach (e.g., 7). The apparent activation energy calculated in this way is 28.5 kcal/mole, which is in very good agreement with a value of 27.9 kcal/mole determined for the HDS of a coal-derived recycle solvent on a carbon-supported molybdenum catalyst (8). These results, particularly the indication of a sequential mechanism involving an initial production of liquids which are subsequently hydrotreated on the molybdenum catalyst, were the experimental basis for probing further into the first step - liquids formation - with particular interest in whether the unusually high concentration of organic sulfur in the Mequinenza lignite might have some effect on the liquefaction behavior.

The C-S bond is significantly weaker than the C-C bond. Although data in various reference sources vary slightly, values of 66 and 83 kcal/mole, respectively, are typical (9). These values were the basis for a hypothesis that a coal structure containing a high proportion of relatively weak C-S bonds may be more easily broken apart, relative to a structure with small concentration of C-S bonds, in either thermolysis or hydrogenolysis. To test this hypothesis the three lignites, with organic sulfur contents ranging from 0.8 to 11.3%, were reacted in both hydrogen and nitrogen atmospheres with and without a catalyst.

The relevant experimental results are summarized in Table 2. The results for reaction in hydrogen atmosphere show that the liquid yield increases as organic sulfur increases, regardless of whether the lignite was first impregnated with a catalyst. Similar results have been reported for other lignites (with the highest organic sulfur content being 6.0%), but that data was obtained at reaction temperatures of 380-460°C (10). The magnitudes of conversions and product yields in the experiments with catalyst and hydrogen gas are comparable to results obtained in the dry (i.e., without added solvent) catalytic liquefaction of a subbituminous coal at comparable reaction conditions (11). For reactions in nitrogen atmosphere, where presumably the decomposition of the coal structure would be due entirely to thermal effects, liquid yield also increased with organic sulfur for experiments in the absence of catalyst. This trend was not followed for reactions in nitrogen with the impregnated molybdenum catalyst, for reasons which are not clear. However, the Cayhiran lignite was the only one of the three to produce measurable quantities of H_2S during the reaction in nitrogen atmosphere, suggesting that the organic sulfur functional groups in this lignite might be different from those of the Hagel and Mequinenza lignites. The composition

of the gas produced in the treatment of the Cayhiran lignite was 77% CO₂ and 23% H₂S, suggesting that some of the sulfur functional groups in this lignite are readily susceptible to catalytic hydrogenolysis directly to H₂S, rather than breaking apart to form sulfur-containing liquids. For example, diaryl disulfides readily undergo reductive cleavage of the S-S bond to H₂S around 300°C (12).

For experiments in the absence of catalyst, both the Hagel and Cayhiran lignites showed an increase in liquid yield for reactions run in hydrogen relative to those run in nitrogen. In the case of the Mequinenza lignite, the liquid yields were essentially identical, within experimental error. This result suggests that the extensive array of C-S bonds enables a facile, thermally induced breakdown of the coal structure which is able to proceed without the intervention of hydrogen.

When reactions were carried out using lignites impregnated with the molybdenum catalyst, a greater yield of liquids was observed, from all three lignites, for experiments in hydrogen relative to those in nitrogen. Furthermore, the improvement in liquid yield, expressed as the difference between the yield in hydrogen and that in nitrogen, itself increased as a function of the organic sulfur content of the lignite. Thus for Hagel lignite the increased liquid yield in hydrogen was 0.7% (i.e., 3.0% in hydrogen vs. 2.3% in nitrogen), while for the Mequinenza lignite the increased yield in hydrogen was 4.5%.

We hypothesize that the key steps which facilitate the formation of liquids in high yield from the high organic sulfur lignites are the generation of thiols and the subsequent role of thiols in cleaving disulfide structures. The relative thermal instability of the S-S bond, which is even weaker (51 kcal/mole) than the C-S bond (13) is offered as an argument that disulfides should not be present in coals, because of the inability of the disulfide group to survive coalification (12). However, the lignites have not experienced extensive coalification. Thiols are easily formed, as for example, by hydrolytic cleavage of disulfides (14) or other organic sulfur functional groups. Once some thiols have been generated in the reaction, they can then facilitate the further reaction of disulfides. A mixture of disulfides and thiols will equilibrate (assuming no species are removed) to produce all possible reaction products; e.g.



If steps are taken to prevent the complete equilibration of the mixture, then the reaction of the thiol with the disulfide can be exploited to achieve essentially permanent cleavage of the latter. In fact, such a disulfide cleavage by thiols is used in biochemical reactions, where such reagents as 2-mercapto-1-ethanol or dithiothreitol (Cleland's reagent) are used to cleave the disulfide linkage in proteins to the free thiol group in cysteine (15). Provided that the disulfide linkages in the lignites are bridging groups, rather than components of cyclic structures (a proviso analogous to the concept of open ethers and closed ethers among oxygen functional groups), the thiols formed by the initial reduction of some of the sulfur groups could then facilitate further depolymerization of the coal structure by reaction with the disulfides.

It has been suggested that organic sulfur is uniformly distributed throughout a coal sample, on the basis of solvent extraction work (16). Specifically, the sulfur content of extracts produced with various solvents is about the same from one solvent extract to another, indicating that even though individual solvents may be able to dissolve different portions, or extents, of the coal structure, approximately the same amount of sulfur is removed in each case. It is also recognized that in dry liquefaction a good dispersion of the catalyst is of special importance in obtaining good conversions (17). The dispersion of the catalyst obtained by the impregnation technique, combined with the inherent dispersion of the sulfur throughout the lignite structure, facilitate the initial reactions of the sulfur functional groups with hydrogen to generate thiols. Even though hydrogenolysis of the disulfide linkages may be continuing throughout the reaction, the cleavage of the disulfide linkage is further enhanced by the disulfide-thiol reaction.

ACKNOWLEDGEMENTS

Dr. Garcia was supported by a postdoctoral fellowship provided by the Spanish Research Council (CSIC). Financial support for the experimental work was provided by The Pennsylvania State University Cooperative Program for Coal Research. The authors are grateful for the sample of Cayhiran lignite provided by the Istanbul Technical University.

LITERATURE CITED

- 1 Garcia, A. B. and Schobert, H. H. *ACS Div. Fuel Chem. Preprints*, **33**(1), 241 (1988).
- 2 Garcia, A. B. and Schobert, H. H. *Coal Preparation* (In press, 1989).
- 3 Yarzab, R. F., Given, P. H., Spackman, W., and Davis, A. *Fuel*, **59**, 81 (1980).
- 4 Neill, P. H., Shadle, L. J., and Given, P. H. *Fuel*, **67**, 1459 (1988).
- 5 Garcia, A. B. and Schobert, H. H. *Proc. 2d Intl. Rolduc Conf. on Coal Sci.* (In press, 1989).
- 6 Garcia, A. B. and Schobert, H. H. *Fuel* (Submitted, 1989).
- 7 Moore, W. J. *Physical Chemistry*, Prentice-Hall, Inc., Englewood Cliffs, NJ (1972), Chapter 9.
- 8 Abotsi, G. M. K. *Ph.D. Dissertation*, The Pennsylvania State University (1987).
- 9 March, J. *Advanced Organic Chemistry*, 3rd ed., John Wiley, New York (1985), p. 23.
- 10 Severin, D., Oelert, H. H., and Yildirim, M. E. *Proc. 1983 Intl. Conf. on Coal Sci.*, p. 52.
- 11 Davis, A., Derbyshire, F. J., and Schobert, H. H. *U. S. Dept. of Energy Report*, No. DOE-PC-90910-3 (1987).
- 12 Tsai, S. C. *Fundamentals of Coal Beneficiation and Utilization*, Elsevier, Amsterdam, (1982) Chapter 5.
- 13 Pauling, L. *College Chemistry*, 3rd ed., W. H. Freeman, San Francisco (1964), p. 316.
- 14 Hudlicky, M. *Reductions in Organic Chemistry*, Ellis Horwood Ltd., Chichester, UK (1986), p. 87.
- 15 Loudon, G. M. *Organic Chemistry*, 2d ed., Benjamin/Cummings, Menlo Park, CA (1988), p. 1170.
- 16 van Krevelen, D. W. *Coal*, Elsevier, Amsterdam (1981), p. 171.
- 17 Hawk, C. O. and Hiteshue, R. W. *U. S. Bur. Mines Bulletin*, No. 622 (1965).

TABLE 1

Ultimate and sulfur forms analyses (dry, ash-free basis) of lignites used in this work.

	Hagel	Cayhıran	Mequinenza
Ultimate			
Carbon	71.34	68.15	64.81
Hydrogen	4.50	5.50	5.72
Nitrogen	1.14	2.21	0.96
Organic sulfur	0.79	4.91	11.32
Oxygen (difference)	22.23	19.23	17.19
Sulfur forms			
Total sulfur	0.93	7.34	12.64
Pyritic sulfur	0.10	1.97	1.15
Sulfate sulfur	0.02	0.52	0.14
Sulfide sulfur			0.04
Organic sulfur	0.81	4.91	11.32

TABLE 2

Results of experiments in hydrogen and nitrogen atmospheres at 275^o, 6.9MPa gas pressure (cold) for 30 min.
 Results are expressed on a dry, ash-free basis.

	Hagel		Cayhıran		Mequinenza	
	H ₂	N ₂	H ₂	N ₂	H ₂	N ₂
Thermal (no catalyst)						
Total conversion	6.0	6.3	4.2	3.0	11.1	11.2
Liquid yield	1.8	1.6	2.4	1.8	11.9	12.1
Gas yield	4.2	4.7	1.9	1.2	-	-
Catalytic						
Total Conversion	7.3	5.5	3.5	1.9	16.0	12.6
Liquid yield	3.0	2.3	3.2	1.8	16.4	11.9
Gas yield	4.3	3.2	0.3	0.1	-	0.7